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Electron beam lithography process using radiation sensitive carboxylate metalorganic precursors

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A bilayer process has been developed for electron beam lithography using radiation sensitive metalorganic precursors as imaging layers in conjunction with organic planarizing layers. Upon electron beam irradiation, the precursor is converted to a metal oxide which serves as an etch mask for subsequent pattern transfer through the planarizing layer. In this article, a titanium(n-butoxide)$_2$(2-ethylhexanoate)$_2$ precursor was investigated that exhibits sensitivity and contrast of 495 μC/cm^2 and 2.75, respectively, 10 keV accelerating potential. The sensitivity was further enhanced to 72 μC/cm^2 using a pre-exposure thermal bake to partially convert the precursor to metal oxide prior to electron beam imaging. Additionally, it was found that combining the titanium(n-butoxide)$_2$(2-ethylhexanoate)$_2$ precursor with a similar precursor containing a higher atomic number metal center, barium(2-ethylhexanoate)$_2$ in this work, also enhanced the sensitivity to 157 μC/cm^2 for a 1:1 molar mixture of the precursors. After imaging and development, the patterns were completely converted to metal oxide by thermal baking to improve the etch resistance of the hard mask. This postdevelopment thermal conversion step was found to result in vertical shrinkage of the features and minimal lateral shrinkage. For bilayer processing, the titanium precursor was imaged on top of hard baked novolac and the pattern was transferred through the novolac using an O_2 reactive ion etch. Sub-100 nm patterning is demonstrated using both single layer and bilayer processes with these materials, with aspect ratios greater than five achieved with the bilayer process. [DOI: 10.1116/1.1624250]

I. INTRODUCTION

Since the early 1980s, electron beam lithography has been considered a potential alternative to optical lithography for critical level patterning in semiconductor manufacturing. However, continued progress in the development of photoresists, optics, and excimer lasers has sustained optical lithography as the principal production lithographic technology. In the near future, 157 nm lithography is expected to be introduced for production of semiconductor devices at the 65 nm technology node.[1] Even with continued advancements and extensions of optical lithography, electron beam lithography continues to play a critical supporting role in semiconductor manufacturing. It is the preferred lithographic method for low volume fabrication that requires high resolution and accuracy such as high resolution mask fabrication[2] and magnetic nanostructures for patterned media.[3] Also, it is extensively used in path-finding research and development of transistor structures beyond conventional metal–oxide–silicon field effect transistors (MOSFETs) such as quantum dots,[4] single electron transistors,[5] and carbon nanotubes.[6]

In electron beam lithography, many of the traditionally popular resists are polymer systems whose dissolution rate increases as a result of a reduction in molecular weight due to chain scission upon exposure to electrons.[7,8] The radical species that can be generated during exposure can also be used to induce rapid crosslinking of a polymer which results in lower dissolution rates.[9] It is this modulation in dissolution rate that permits the formation of a relief image in these materials. Another approach by which to bring about solubility changes is through transfer of incident electron energy to a photoacid generator (PAG) contained within a chemically amplified resist, and it is the production of acid in these systems that catalyzes reactions responsible for providing contrast.[10] All of these aforementioned approaches utilize organic polymers with low atomic number species such as carbon, oxygen, and hydrogen. Recently, many groups have been pursuing the use of high atomic number species in electron beam resists in order to improve etch resistance, sensitivity, and contrast while retaining high resolution. For example, spin on glasses such as hydrogen silsesquioxane (HSQ) crosslink upon electron beam irradiation and provide excellent resolution.[11] Here, we report on a process for directly patterning metal oxides through electron beam irradiation of metalorganic precursors.

In this approach, electron beam irradiation of the precursor results in cleavage of organic ligands from the metal center to create an unstable molecule that can further decompose and form a metal oxide. Additionally, these precursors exhibit strong absorption bands in the deep ultraviolet region which permit optical patterning and these materials can be converted to metal oxides using low temperature bakes. During the conversion process, organic species are removed from the precursor which results in the subsequent formation

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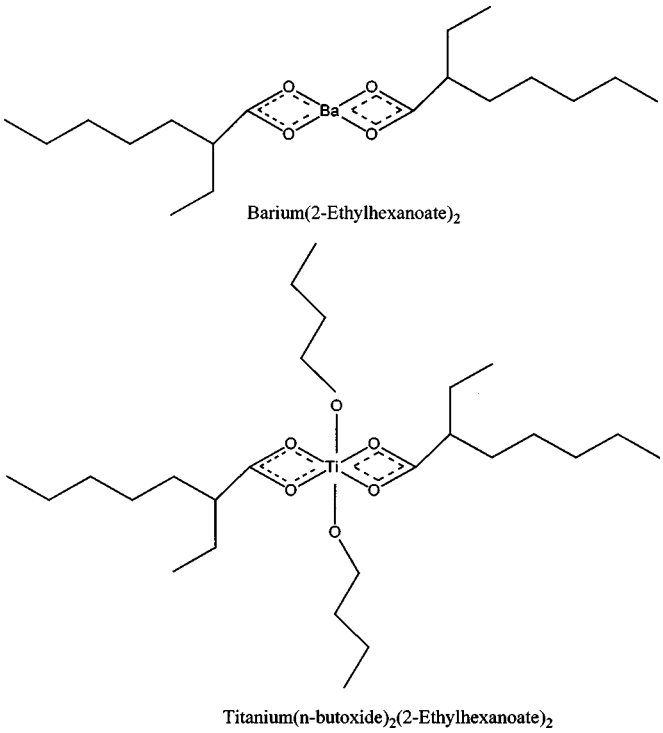

FIG. 1. Molecular structures of barium(2-ethylhexanoate)$_2$ and titanium(*n*-butoxide)$_2$(2-ethylhexanoate)$_2$.

of a metal oxide network that eventually is no longer soluble in organic solvents.[12] After patterning the unexposed regions can be removed using a standard organic solvent as a developer to delineate the metal oxide patterns. Finally, the delineated patterns can be fully converted to the metal oxide through thermal baking or radiation exposure in order to enhance the etch properties and other characteristics of the metal oxide patterns. In this article, the use of carboxylate precursors of both titanium and barium as electron beam imaging layers is reported.

II. EXPERIMENTAL DETAILS

The molecular structures of the barium(2-ethylhexanoate)$_2$ and titanium(*n*-butoxide)$_2$(2-ethylhexanoate)$_2$ precursors used in this work are shown in Fig. 1. Precursor films were spin coated from methyl isobutyl ketone (MIBK) onto silicon substrates and soft baked at 90 °C for 90 s to form high optical quality films with thickness uniformity below 2%. The thickness and uniformity of the resulting films were measured using a variable angle spectroscopic ellipsometer (J. A. Woollam Co.). Ellipsometry data, Ψ and Δ, were collected from 400 to 1100 nm at a spacing of 10 nm and at three different angles (65°, 70°, and 75°). The thicknesses and optical properties of the films were determined from this ellipsometry data using the WVASE32 software package (J. A. Woollam Co.) by modeling the metalorganic film as a single Cauchy layer.

Electron beam exposures were performed using a JSM 5910 scanning electron microscope (SEM) (JEOL Ltd., Tokyo, Japan). Pattern generation and control were performed using Nabity Pattern Generator Software (NPGS) and hardware from J. C. Nabity Systems. Electron beam focus and astigmatism were optimized using evaporated gold on polished pyrolytic graphite purchased from E. F. Fullam, Inc., Latham, NY. The beam diameter was determined to be approximately 5 nm at an accelerating potential of 25 keV. All exposures were performed using a beam current of 10 pA and SEM magnification of 1000 (which produces a writing field size of $100\times100\ \mu$m). For contrast curve measurements, dose arrays of 10 μm square pads were exposed, developed in MIBK, and their step heights were measured using a Dimension 3100 atomic force microscope (AFM) with a Nanoscope IIIa controller (Digital Instruments, Santa Barbara).

For bilayer lithography processing, novolac was spin coated onto silicon substrates and hard baked at 180 °C for 2 h to crosslink and harden the film. A metalorganic film was then spin coated onto the hard baked novolac film and soft baked at 90 °C for 90 s. After electron beam imaging, a spin development protocol was used to develop the metalorganic imaging layer. Fresh developer was dispensed onto the wafer while spinning at 200 rpm for 30 s and dried at 1000 rpm for 60 s. Finally, a PlasmaTherm reactive ion etcher (RIE) was used with O_2 gas at a flow rate of 40 sccm at 200 W and 50 mTorr to transfer the patterns through the underlayer.

III. RESULTS AND DISCUSSION

A. Sensitivity enhancement

A unique aspect of these precursors is that they respond to both optical irradiation and low temperature thermal baking in addition to electron beam irradiation. In the early history of these materials, one of the objectives was to develop a directly photodefinable high dielectric constant material for use in fabricating integral capacitors and other dielectric layers in high density packaging applications.[12] These metalorganic precursors show strong optical absorption bands in the deep ultraviolet region. For example, the titanium(*n*-butoxide)$_2$(2-ethylhexanoate)$_2$ precursor exhibits optical sensitivity of approximately 687 mJ/cm^2 and contrast of 5.68 upon exposure to 248 nm light. These precursors can also be blanket converted to metal oxide through thermal baking at moderate temperatures ($<$200 °C) for relatively short times ($<$1 h). These advantages allow processing flexibility where the precursor can be partially or fully converted using either or combinations of these different methods.

Through the use of photochemical or thermal conversion as an initial partial conversion step, the electron beam dose required to pattern these precursors can be reduced. In this work, enhancement of the sensitivity of the titanium carboxylate precursor was investigated using pre-exposure thermal bakes at 150 °C for 1, 2, and 3 min. For these experiments, a nominal film thickness of 440 nm was used. The contrast curve measurements were performed with film thicknesses above 400 nm to ease in measurement of the step heights using the AFM. However, hard mask applications for electron beam lithography require film thicknesses less than

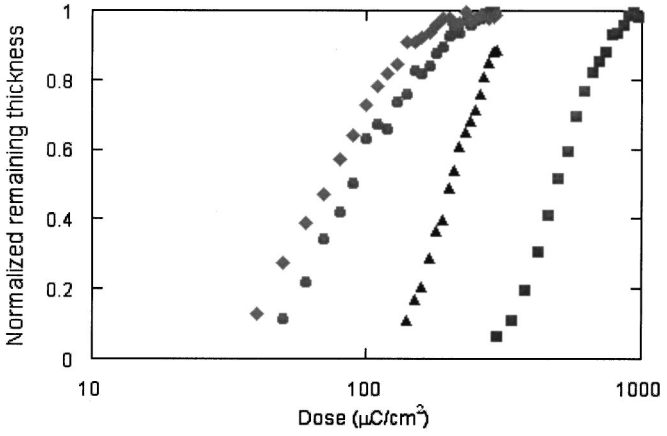

FIG. 2. Sensitivity enhancement of the titanium(*n*-butoxide)$_2$(2-ethylhexanoate)$_2$ precursor using a thermal bake at 150 °C for 0 (squares), 1 (triangles), 2 (circles), and 3 (diamond).

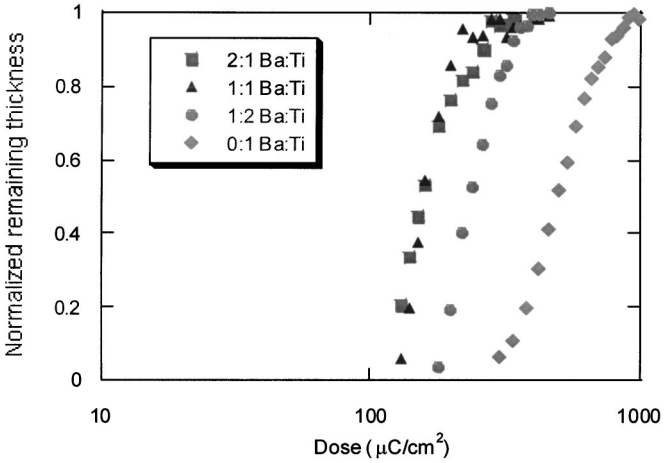

FIG. 3. Contrast curve data for mixtures of barium(2-ethylhexanoate)$_2$ and titanium(*n*-butoxide)$_2$(2-ethylhexanoate)$_2$ precursors.

100 nm. Figure 2 shows the response curves for the different thermal treatments followed by electron beam irradiation. Here, sensitivity has been defined as the dose required to produce development of half the initial film thickness after exposure and contrast $[\gamma = 1/\log(D_{100}/D_0)]$ where D_0 and D_{100} are the doses at 0% and 100% of the normalized remaining thickness after development, respectively. As expected, the sensitivity was enhanced with longer pre-exposure bake times as a result of larger extents of conversion from the precursor to the metal oxide. The sensitivity was enhanced from 495 to 200 μC/cm^2 while the contrast remained roughly constant at 2.7 for 1 min of pre-exposure thermal baking. With 2 min of pre-exposure thermal baking, the sensitivity was further enhanced to 90 μC/cm^2 but the contrast decreased to 1.4. Also, a pre-exposure thermal bake of 3 min resulted in sensitivity and contrast of 72 μC/cm^2 and 1.3, respectively. It should be noted that the film cannot be fully and cleanly developed beyond 3 min of thermal baking at 150 °C. The main disadvantage of using pre-exposure thermal baking is that a reduction in contrast is observed with longer bake times. Without pre-exposure thermal baking, the difference in the extent of conversion between exposed and unexposed is highest, and leads to the largest contrast. Pre-exposure thermal baking enhances the sensitivity of the film by partially converting the precursor to metal oxide throughout the entire film, thus changing the film into a form that is closer to its point of insolubility in the developer. Unfortunately, this isotropic conversion also reduces the ultimate difference in the extent of conversion between the exposed and unexposed regions of the patterned film which then results in decreased contrast with an increase in thermal bake times.

B. Effects of high atomic number species

The use of high atomic number species with large electron clouds can promote the generation of a larger number of secondary electrons. Therefore, it was postulated that the addition of higher atomic number species to the film could possibly be used to enhance the sensitivity of the imaging layers. In this work, a preliminary investigation of the effect of adding a second metalorganic precursor which contains a higher atomic number metal species on the sensitivity of the resulting imaging material was conducted. In this work, a barium(2-ethylhexanoate)$_2$ precursor was chosen since it contains the same chelating ligand as the titanium precursor, which plays the primary role in the decomposition of the precursor to metal oxide upon exposure. The impact of the addition of the high atomic number metal species was studied by imaging different molar combinations of barium and titanium precursors. It was not possible to image a pure barium(2-ethylhexanoate)$_2$ film since that precursor could not be coated into a high quality film. Precursor films of 2:1, 1:1, and 1:2 molar ratios of barium to titanium precursor were spin coated to thicknesses of approximately 500 nm. The contrast curves for the various mixtures exposed at 10 keV accelerating potential are shown in Fig. 3. The titanium(*n*-butoxide)$_2$(2-ethylhexanoate)$_2$ precursor by itself exhibits sensitivity of 495 μC/cm^2 and contrast of 2.7. With the addition of barium(2-ethylhexanoate)$_2$ precursor in a Ba:Ti molar ratio of 1:2, the sensitivity was enhanced to 237 μC/cm^2 while the contrast increased to 3.8. The 1:1 Ba:Ti molar mixture exhibited enhanced sensitivity and contrast of 157 μC/cm^2 and 4.9, respectively. However, further addition of the barium(2-ethylhexanoate)$_2$ precursor in a Ba:Ti molar ratio of 2:1 exhibited similar sensitivity of 157 μC/cm^2 and decreased contrast of 3.9. Thus, it was found that the addition of a higher atomic number metal precursor could be used to enhance the sensitivity of the imaging layer considerably. The optimal ratio for the titanium and barium precursors used in this work was found to be approximately a 1:1 Ba:Ti molar mixture.

C. High resolution direct and bilayer patterning of metal oxides

The ability to directly pattern titanium dioxide films may have application in a variety of technologies including solar cells[13] and optical waveguides.[14] The titanium metalorganic precursor used in this work provides an approach for obtain-

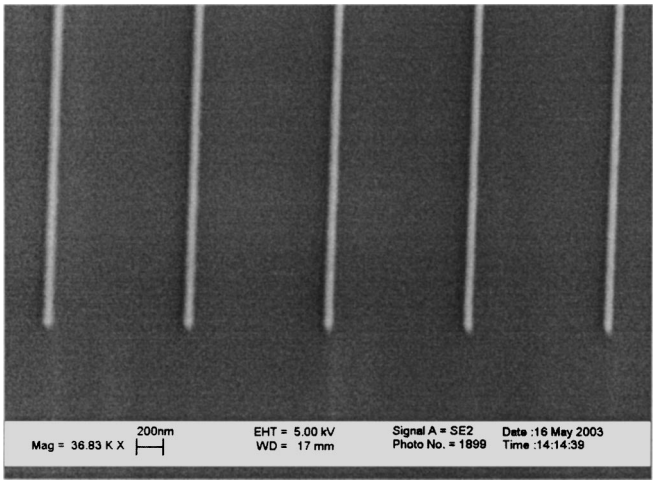

FIG. 4. Sub-100 nm single layer patterns produced on a silicon substrate by electron beam lithography using a 180 nm thick titanium(*n*-butoxide)$_2$(2-ethylhexanoate)$_2$ precursor film.

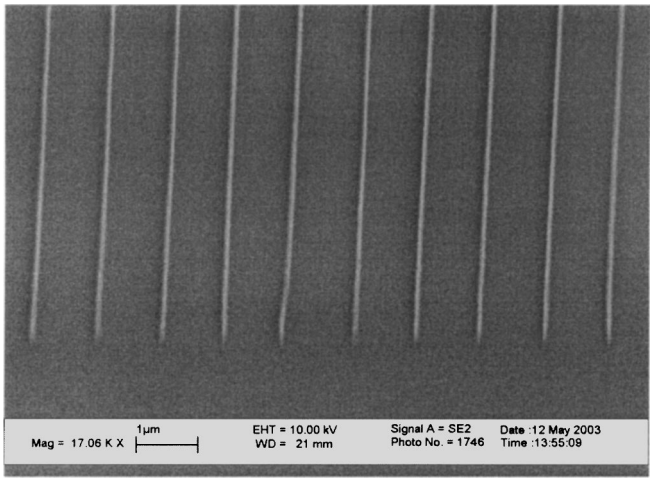

FIG. 6. Bilayer structures produced by imaging a titanium(*n*-butoxide)$_2$(2-ethylhexanoate)$_2$ film on a hard baked novolac planarizing layer and pattern transferring the structure using oxygen plasma.

ing patterned titanium dioxide structures. Multiple pass, single line electron beam exposures using 20 nm pixel-to-pixel spacing were performed at an accelerating potential of 25 keV. A 180 nm thick titanium precursor film was coated and exposed on a silicon substrate and developed with the spin development protocol discussed previously using MIBK. Figure 4 shows a top down view of sub-100 nm isolated lines printed at 1500 μC/cm^2. After development, these patterns can be fully converted to the titanium dioxide through optical irradiation or high temperature thermal baking. During this conversion process, the pattern will shrink somewhat as organic ligands are removed from the structures. AFM was used to investigate the patterned film shrinkage caused by postdevelopment thermal baking. A large 500 nm pattern array was exposed at 1000 μC/cm^2, developed in MIBK for 30 s, and scanned before and after thermal baking at 180 °C for 15 min. The AFM images of the resulting structures are shown in Fig. 5. It is observed that thermal baking of the imaged pattern results in vertical shrinkage and minimal lateral shrinkage. The shrinkage is dependent upon the extent of conversion achieved through electron beam irradiation. For the electron beam exposure and thermal treatment performed here, it was found the patterns shrunk vertically by about 35 nm.

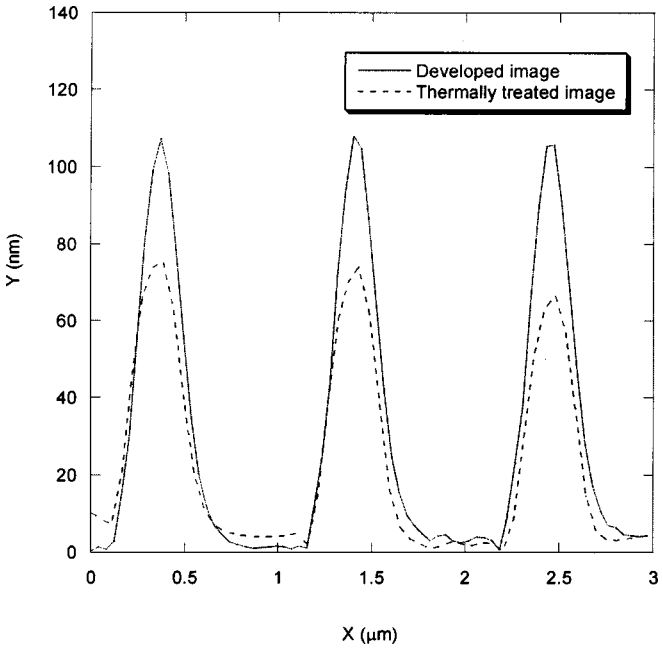

FIG. 5. AFM cross-sectional profiles of a 500 nm line/space array imaged in the (*n*-butoxide)$_2$(2-ethylhexanoate)$_2$ precursor using a dose of 1000 μC/cm^2 before and after postdevelopment baking at 180 °C for 15 min.

Bilayer lithography was performed using hard baked novolac as the planarizing layer. A 110 nm thick titanium precursor film was spin coated on top of a 430 nm thick hard baked novolac layer. After exposure and spin development in MIBK, the etch mask was thermally baked at 180 °C for 30 min to ensure full conversion to metal oxide. Finally, the metal oxide pattern was transferred through the hard baked novolac layer using an O_2 reactive ion etch. It should be noted that, during this work, the inclusion of argon in the etch gas mixture, which would normally be used to improve the anisotropic nature of the plasma, was found to damage the etch mask and result in redeposition of metal oxide debris. The etch rate of the hard baked novolac in the oxygen plasma was 5 nm/min and a 5% overetch was performed. The etch selectivity of the thermally converted sample for 30 min at 180 °C compared to hard baked novolac was greater than 100:1. Figure 6 shows a tilted SEM image of isolated bilayer patterns printed using 1800 μC/cm^2. The linewidths of the feature are 100 nm with an aspect ratio of approximately 5.

IV. CONCLUSIONS

The use of titanium and barium carboxylate metalorganic imaging layers was investigated and demonstrated for electron beam lithography. It was found that inclusion of a higher atomic number species, barium carboxylate, with the tita-

nium precursor could be used to enhance the sensitivity and contrast of the imaging layer. It was also shown that the titanium precursor sensitivity could be enhanced using preexposure thermal baking, but that prolonged baking resulted in a decrease in contrast. The use of postdevelopment baking, which can fully convert the metal oxide patterns and improve their etch resistance and other properties, was shown to result in vertical shrinkage of the imaged patterns and minimal lateral shrinkage. Finally, sub-100 nm patterning was demonstrated in both single layer and bilayer lithography processes using titanium(n-butoxide)$_2$(2-ethylhexanoate)$_2$.

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